Cold Regions Research and Engineering Laboratory

Point-Source Energetics Detection: Initial Sensor Evaluation

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April 2004

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Prepared for   U.S. ARMY CORPS OF ENGINEERS

ABSTRACT

The development of real-time detection capability for explosives and propellants in high-concentration point sources is an important objective for comprehensive test and training range management. This report documents efforts to identify and characterize sensors that are both sensitive and selective to high-concentration point sources and can operate in a standoff mode by detecting the vapors released by energetics. Other factors under study included portability, speed of analysis, and overall system ruggedness. Initial evaluations identified 28 potential detection systems. Based primarily on sensitivity requirements, the initial list was reduced to five candidate detectors. The subset of detectors was then subjected to further evaluation, including extensive laboratory testing. Based on the results of laboratory testing and evaluations, we identified a single detector that warrants further investigation: GE Ion Track's Vapor Tracer[2]. The Vapor Tracer[2] is the most sensitive of the detectors tested and has the greatest freedom from interferences. We recommend follow-on laboratory and field investigations to determine the potential of this detector for high-concentration point-source detection.

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PREFACE

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The commander and executive director of the Engineer Research and Development Center is COL John W. Morris III, EN. The director is Dr. James R. Houston.

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1   PURPOSE

The overall objective of this work unit is to develop a real-time detection capability for locating chunks of high explosives and propellants and zones of high concentration in soil. Surveying currently available explosives detectors, focusing primarily on their inherent sensitivity and selectivity, was the first goal. From the broad list of detectors identified, the most promising candidates were selected for in-house laboratory testing. From these testing results, a single detector, which possesses the highest likelihood of providing real-time sensing capabilities, was selected and will be advanced for more extensive laboratory and field testing.

2   BACKGROUND

Previous characterization studies have indicated that the major deposits of explosives residues at Army test and training ranges are located as finite point-source zones near targets, where low-order (partial) detonations have taken place (Jenkins et al. 2000, Hewitt et al. 2003). In these areas, large pieces of shrapnel may contain substantial residues of undetonated explosives. Chunks of unassociated explosives are often ejected from the detonation fireball. Fine particles of explosives that are not visible to the unaided eye may contaminate the surface soil to percent levels. For ranges in the arid west, these zones may sometimes become visible as weathering processes turn many energetic residues to a distinctive red-orange color. In moist, heavily vegetated areas, it is nearly impossible to locate these source zones at present. The ability to easily detect major deposits of energetic material would allow range managers to implement best-management practices to enhance range sustainment by locating and remediating major source zones of contamination before the material dissolves and enters the hydrologic cycle.

On-site, real-time, portable detectors were assessed with regard to their ability to detect high concentration sources. The DARPA Dog's Nose program developed several sensors that were not sufficiently sensitive to detect buried land mines, but may be adequate for detecting high concentrations of explosives and propellants on the soil surface. Other detectors have been developed for use in screening passengers and luggage for explosives at airports. Several candidate detectors were available in portable, battery-operated formats, including the Nomadics Fido system and several commercially available ion-mobility spectrometers. These and other candidate sensors were evaluated in the laboratory against various explosive vapors to provide performance characteristics. The most successful of these sensors will be field tested at several types of training ranges to assess whether they provide adequate sensitivity for this application. If the detection capability is adequate, field tests will evaluate whether the detectors are practical for various terrain and vegetative cover scenarios. Specific protocols will be developed for use at different types of Army ranges.

Although none of the sensors can detect RDX because of its low vapor pressure, nearly all Army energetics compositions that contain RDX also contain TNT. Thus, locating and treating areas with RDX contamination will most likely be possible by locating the TNT.

Evaluation Criteria

To compare the potential of vapor sensor technologies in our initial evaluation, we investigated the following attributes of the available detector systems: sensitivity, selectivity, maturity, and compatibility with the prospective field detection scenarios. As with any chemical measurement, adequate sensitivity and selectivity were the principal criteria for establishing the proper methodology. Furthermore, the selectivity had to be sufficiently high to ensure that positive or negative interferences expected on ranges would not adversely affect the detection of the target analytes. The sensitivity criterion dramatically reduced the number of candidate sensors, as many did not approach the target detection limit. In addition to detection performance measures, it was important to assess the maturity and utility of the systems within the constraints of point-source energetic delineation.

Initial Evaluation of Available Technologies

We conducted a comprehensive evaluation of current technologies for detecting explosives vapors to facilitate the selection of candidate systems to be tested. Our selection process relied on building a database of the commercially available chemical explosives sensors that were nominally capable of detecting concentrations in the part-per-million (v/v) range. The broad range of detectability was considered since detector configurations that were seemingly not sensitive enough might be made so with limited modifications. Through our assessment, we identified 28 detection systems offered from 16 manufacturers (Appendix A). The primary sources of information for our initial assessment included in-house knowledge of the state of the art in explosives detection systems, recent review articles, and World Wide Web searches. In addition, we acquired important information on available detectors through telephone conversations with technical representatives and sensor developers. Sensor systems were categorized by their operating principles and detection limits.

The sensor systems identified represent a wide spectrum of analytical technologies. These range from ion mobility spectrometry (IMS), to gas chromatography (GC) with surface acoustic wave (SAW) detection, to fluorescence-quenching polymers. In our initial search, we found that many technologies were in the development stage, while others were being phased out and replaced by more current technologies.

After selecting the detectors that met the sensitivity and selectivity criteria, we obtained more precise information about the detection capability of selected sensors through telephone conversations with sensor manufacturers. The primary objective of these contacts was to establish a reliable limit of detection for each

detector. It was also important to determine the particular chemical compounds and units of measurement (e.g., by volume/volume or by mass/volume). A secondary objective was to acquire technical and operational details for each detector. This information included sampling modes (i.e., particle or vapor), sampling time, sample volume, analysis time, and any special analytical considerations, as well as specifications on the detector size and portability. These direct interviews with sensor developers proved extremely useful and in many cases clarified published information that was either ambiguous or incomplete. A summary of the initial survey is presented in Appendix A.

The complete set of detectors was then carefully evaluated with all of the available data for their potential as point-source detectors. The five candidate detectors listed in Table 1 were initially chosen for further laboratory evaluation, and the list was subsequently reduced to three systems after closer investigation:

- zNose from Electronic Sensor Technology;
- Vapor Tracer[2] from GE Ion Track; and
- FIDO from Nomadics.

These were chosen because of their sensitivity, maturity, and availability.

While laboratory evaluations were being conducted on the first three detectors, additional information was obtained on the remaining systems. The Ion Trap Detector/Mass Spectrometer (ITD or ITMS), while being extremely sensitive, did not posses a mature sampling system specifically optimized for explosives detection. The sampling system most likely will be developed in future work. Further investigation of the Thermo Detection EGIS II/III system, which operates on the principle of gas chromatography with chemiluminescence (GC/CL) detection, indicated that it was primarily a fixed laboratory instrument and was not suitable for deployment on a range. Additionally, the manufacturer of this detector was not very responsive to the needs of our work. This information resulted in the decision not to evaluate these detectors at this time.

Table 1. Candidate point energetics sensors.

Manufacturer	Model	Technology	TNT detection limit (mass)	TNT detection limit (v/v)
Electronic Sensor Technology	zNose	GC/SAW	10 pg	
GE Ion Track	Vapor Tracer[2]	IMS	10 pg	
Nomadics	FIDO	QFP		6.0 ppt
Varian / ORNL	Saturn	ITD	500 fg	
Thermo Detection	EGIS II/III	GC/CL	50 pg	

(pg – picogram, fg – femtogram, v/v – volume/volume, ppt – parts per trillion)

3   DESCRIPTION OF CANDIDATE VAPOR DETECTORS

FIDO

The Nomadics FIDO is a portable, hand-held explosives vapor detection system that was specifically designed for detecting landmines. The instrument's primary response is to trinitrotoluene (TNT), although it also responds to 2,4-DNT and other nitroaromatics. The detector provides a single output signal that is a composite of all responding chemicals.

In FIDO, detection is based on quenching of a fluorescence polymer (QFP). A highly fluorescent moiety is synthesized into a conjugated polymer and dispersed in a thin film of polyisobutylene. The fluorescent moiety is chosen so that it has a strong interaction with TNT, where the interaction decreases the fluorescent intensity. The fluorescence quenching is amplified through the conjugated backbone so that a single TNT molecule can lead to the quenching of numerous fluorescing units.

The sampling rate is variable up to 30 mL/min. The fluorescence-quenching signal is cumulative and develops slowly, requiring up to 60 s for low-level analysis. The temperatures of the inlet and polymer are also important variables that affect the instrument response. Nomadics is developing a number of polymer formulations and film thicknesses in an effort to enhance the sensitivity and shorten the response time.

Vapor Tracer[2]

The Vapor Tracer[2] is a portable, hand-held explosives vapor detection system that responds to a broad range of explosives, including 2,4-DNT, TNT, and nitroglycerine. The system is lightweight and is operated through a well-developed and flexible user interface. The associated explosives-detection software is robust and contains sophisticated alarm functionalities.

Detection in the GE Ion Track Vapor Tracer[2] is based on quantifying the mobility of different ions at atmospheric pressure. During the measurement process, sample vapors are passed over a nichrome wire helix that adsorbs and preconcentrates nitroaromatic compounds preferentially over interfering vapors. The nitroaromatics are thermally desorbed and diffuse through a dimethyl-polysiloxane (silicone) membrane into an ionization chamber. Analytes are then chemically ionized via proton abstraction using an abstraction agent such as methylene chloride and are then negatively charged by electron capture of [63]Ni

beta emission. The charged species are then propelled into a drift tube by an electric field, where the ions are ultimately counted with a Faraday cup. Analytes are distinguished by their drift times, which are proportional to their molecular weights.

The sampling rate is fixed at 4000 mL/min, and sampling times are variable up to 100 seconds. Typical sampling times are 10 s. IMS analysis times are variable up to 15 s, where 3-s read times are usually sufficient.

zNose 4100

Electronic Sensor Technologies (EST) zNose 4100 is a small vapor sampling and analysis device. The detector can analyze a wide range of analytes in a single sample by separation on an internal gas chromatograph. The unit consists of two major components: a base station (roughly the size of a large suitcase), and a GC/SAW (gas chromatograph/surface acoustic wave) module (roughly the size of a briefcase) connected by an electronics and carrier gas line. The system also requires a PC for instrument control and data display and manipulation. The system requires AC electrical power and UHP (ultra-high-purity) helium.

The zNose relies on a GC with a SAW microbalance detector. During the sampling process, vapors are passed through a small Tenax preconcentration trap and then thermally desorbed. Desorbed analytes are directed into a temperature-programmed GC utilizing a 1-m capillary column. The column effluent condenses on the small, thermoelectrically cooled surface of the SAW microbalance. The SAW device measures the resonant frequency of the cooled detector surface, which is a function of the mass of material deposited on the surface. The raw data appear as the accumulated mass of analytes versus time. Data reduction algorithms produce a familiar-looking chromatogram of analyte peaks versus time. The SAW surface is reconditioned for each subsequent analysis by thermal desorption.

The sampling rate is fixed at 15 mL/min, and sampling times are variable up to 100 s. Typical sampling times during our tests were approximately 30 s. GC/SAW analysis times are also user selectable but are generally in the range of 10–20 s, followed by a 30-s detector surface bake and subsequent cooldown.

4   LABORATORY TESTING OBJECTIVES

The objective of our laboratory evaluations was to characterize the analytical performance and usability of the candidate vapor sensors for point-source energetics delineation. The primary performance characteristics were sensitivity to explosive compounds and selectivity, i.e. freedom from interference from non-target compounds. Additional characteristics included speed of analysis, freedom from carryover (memory effects), and calibration stability. Usability characteristics were assessed for effectiveness of the user interface for instrument control and data display and manipulation, system durability, maintenance requirements, start-up times, and calibration stability. Also of concern were physical dimension, weight, power consumption, special environmental limitations (e.g., humidity), and level of support available from the manufacturer.

While the sensors must ultimately perform outdoors where various environmental factors (e.g., temperature, humidity, airborne particulates) complicate the measurement process, an initial laboratory characterization was valuable to ascertain the ultimate or best-case performance of the sensors.

5   TEST LIMITATIONS

Environmental Factors

Our tests were conducted in a controlled laboratory environment; hence, the effect of severe environmental conditions on detection and selectivity remains unknown. Environmental factors not tested included wind, rapid or extreme temperature fluctuations, rapid or extreme changes in humidity, and the effects of direct or indirect sunlight.

Analytical Factors

Standards and samples were introduced into each detector using their native sample introduction systems, with the exception of the Vapor Tracer[2], where a snorkel sampler was used. This snorkel was custom-made for this detector by attaching a short length of appropriately sized tygon tubing to the sensor inlet and inserting the free end into the vapor space of a narrow-mouth glass bottle containing known concentrations of explosives vapors. For FIDO (30 mL/min sampling rate for 1.0 minutes, resulting in a total sample size of 30 mL) and zNose (15 mL/min sampling rate for 30 s, resulting in a total sample size of 7.5), the dilution effect in sampling an 800-mL gas sample was considered negligible. For Vapor Tracer[2] (4000 mL/min sampling rate for 10 s, resulting in a total sample size of 670 mL), standards were analyzed from both 800- and 3200-mL volumes.

6   TEST AND EVALUATION APPROACH

All testing and related activities were conducted in the analytical chemistry and explosives testing laboratory at ARA's facilities in South Royalton, Vermont. Experimental tests were performed in a systematic manner to evaluate analytical performance (e.g., sensitivity and selectivity) and usability factors (e.g., data display and interface, instrument start-up, maintenance, failure, and recovery). Henry's Law constants and aqueous solutions of explosives for preparation of the vapor standards were supplied by Dr. Thomas Jenkins at ERDC/CRREL.

Analytical Performance

Sensitivity is defined as the minimum concentration of target analyte that can be reliably detected. For vapor-phase samples, concentrations can be expressed either as mass per unit volume or as volume per unit volume. In general, the results presented here express concentrations as volume per unit volume. To evaluate each detector's response and ultimate detectability, vapor standards of decreasing concentration were introduced into the detector and its responses were measured.

Each detector has a variable sample volume derived from variable sampling times and/or sampling rates. The analysis time can also be varied. Because the test and training range areas that must be surveyed is large, the total analysis time is important; total analysis times of less than one minute are considered favorable. However, with variable sampling and analysis times, there must be a compromise between sensitivity and total analysis time.

Selectivity evaluations provide information regarding the behavior of a detection system in the presence of common contaminants. Of particular interest to the military are the responses of detectors to gasoline and diesel combustion vapors. The general method for assessing the effects to petroleum byproducts was to obtain samples of the interferent gases and expose the detectors to them in the same manner as the vapor standards.

Vapor standards of TNT and 2,4-DNT were prepared using the vapor pressure of these analytes over aqueous solutions. Henry's Law gives the relationship between vapor pressure and solution concentration. Henry's Law constants were measured for TNT and 2,4-DNT at ERDC/CRREL. The Henry's Law constants used for this study are given in Appendix B.

Standards of varying concentrations were made at two volumes: 800 and 3200 mL. The 800-mL volume standards were prepared by adding 200 mL of aqueous TNT or 2,4-DNT standard to a 1000-mL bottle, while 3200-mL vapor standards were prepared by adding 800 mL of aqueous standard to a 4000-mL bottle. All standards were capped and equilibrated before and between uses.

Usability

The usability of the detectors tested in laboratory was documented along with the results of performance tests. Observations were made with regard to the functionality and stability of the data system, detector maintenance and start-up, and issues arising from failures requiring manufacturer support.

7   EVALUATION RESULTS

Analytical Performance

Sensitivity

Sensitivity was evaluated using vapor standards. Parameter settings, which varied for the different detectors, were chosen to enhance each detector's ability within the guidelines of reasonable analytical cycle times and sampling rates and volumes. For this work the maximum total analysis cycle was set at two minutes, and the maximum sample volume was set to 1 L. Table 2 summarizes the results of the sensitivity tests.

Table 2. Detection limit and related detector parameters.

Detector	TNT detection limit (ppt v/v)	Sample size (mL)	Sample time (s)	Analysis time (s)
FIDO	30	30	60	60
Vapor Tracer[2]	10	670	10	10
zNose	500	7.5	30	40

FIDO repeatedly detected a 112-ppt standard but could not detect an 11-ppt standard. Given the signal strength and reproducibility of the 112-ppt standard versus the control standard (distilled water), the detection limit was estimated at 30 ppt. The temperature of the polymer in the FIDO detector had been reduced to $40°C$ to provide maximum sensitivity at the expense of analytical speed. The full analysis cycle for FIDO was approximately two minutes, the maximum considered acceptable. FIDO required a 30-mL vapor sample.

Within the parameters of our tests, the Vapor Tracer[2] exhibited the greatest sensitivity to TNT. An 11-ppt (v/v) standard was almost always detected when exposed to the instrument. The Vapor Tracer[2] also exhibited the fastest analytical time cycle and utilized the largest sample volume.

The zNose detector was able to detect TNT standards at 900 and 450 ppt, and the lower detection limit was estimated to be 500 ppt. The zNose was the least sensitive of the detectors examined, partially because of a low sampling rate of 15 mL/min. Longer sampling times, for example 60 s, would lower the detection limit and yet remain within the maximum allowable analysis cycle time.

Experiments that we conducted showed that a strong relationship exists between sampling time and signal strength. From this we predicted a detection limit at a 120-s sampling time to be 250 ppt.

The VaporTracer[2] also has a unique feature that virtually eliminates carry-over from previous samples that may have had high concentrations of the target analyte(s). After an analysis cycle and the display of the results, this system automatically heats the preconcentrator and reads addition sample data. If the data indicate that the system is clean, the system notifies the user that it is free from carryover and ready for the next analysis. If the system senses contamination, it continues in a desorb and analysis cycle until the system is clean.

Another useful attribute of the Vapor Tracer[2] is the potential to sample large volumes in a relatively short time. For chunk energetics and high-concentration soils, explosives-containing vapors will be highly localized near the surface of the soil over and around the contamination. A sampling shroud might be used to delineate a vapor sampling volume. A 20-cm-diameter and 10-cm-high shroud contains 3200 mL of vapor. This entire volume can be sampled and analyzed by the Vapor Tracer[2] in one minute. The FIDO and zNose would require over 100 minutes to sample the same volume over the same area.

Since 2,4-DNT is a component of single-base propellants and a manufacturing impurity in TNT, we determined the relative response of TNT to 2,4-DNT for each detector. The relative response is a ratio of the detector's response to TNT compared to its response to 2,4-DNT (Table 3). Note that the relative response to 2,4-DNT is much lower than the response to TNT for each of the detectors, even though the vapor pressure of DNT is substantially higher than that of TNT.

Table 3. Relative response of TNT to 2,4-DNT for the three vapor detectors.

Detector	TNT / 2,4-DNT
FIDO	80
Vapor Tracer[2]	80
ZNose	10

Selectivity

Selectivity experiments were performed to measure each detector's response to common vapor interferents that are expected to occur during range surveys.

These are water vapor, gasoline combustion exhaust, and diesel combustion
exhaust. The detectors exhibited a wide range of responses from virtually no
response, as was the case with the Vapor Tracer[2], to instrument failure, as was
the case with FIDO and the zNose 4100 when exposed to diesel exhaust. The
apparent TNT response for each interferent is presented in Table 4.

Table 4. Apparent TNT response to interferents in [ppt (v/v)].

Detector	Water vapor	Gasoline exhaust	Diesel exhaust
FIDO	5	200–400	~1000 *
Vapor Tracer[2]	No response	No response	No Response
zNose	No response	No response	Detector shutdown

* Irreversible response due to polymer degradation.

FIDO was also exposed to several single-component chemical standards. The
chemicals and their vapor concentrations were benzaldehyde at 23 ppb, benzo-
quinone at 60 ppb, and benzonitrile at 500 ppb. None of these vapors produced
an apparent response at the given concentrations.

Usability

Data System

Instrument control and data display programs for FIDO are run on a Palm
Computer. We found adequate control over instrument settings and relatively
easy access to data relating to the detector's state (e.g., polymer temperature).
The data system provided a means to view the detector's response in real time.
The version of the FIDO detector we tested did not contain any explosives identi-
fication algorithms and nor any alarm mechanisms.

Instrument control and data display for the Vapor Tracer[2] are primarily
controlled from a microprocessor-controlled LED interface built into the detector
unit. There are also additional advanced data displays and storage available from
programs running on an optional PC. All system controls were easily accessed.
The primary data display reported multiple explosives substances using a bar
chart format. In addition, this system has sophisticated explosives identification
and alarm functionally, where specific substances can be set to trigger the alarm
at differing concentrations. The data system was extremely robust and did not
exhibit any anomalies or failures.

The zNose instrument control and data display programs run on an external PC. All instrumental control was accessed from the main program and was straightforward to manipulate. Data display and data manipulation functionality are extensive, as is expected because the zNose detector is a general analytical tool that can be applied to many analytical situations. Alarm mechanisms were built in and easily set. However, there were substantial issues related to maintaining communications between the control computer and the instrument on a day-to-day basis. Restarting both the computer and the analyzer cleared these control issues. In addition, the data system would occasionally "hang" for other unknown reasons.

Start-Up and Maintenance

Nomadics recommends changing the polymer capillary on the FIDO after every four hours of operation. The fluorescence yield of the polymer decreases with time, principally because of photo-degradation from the excitation source and irreversible interactions with sample analytes and their matrix. The process of changing the capillary is simple and can be completed in less than five minutes. Once a new capillary is in place, the system can be powered up and temperature set points entered. Generally, with a new capillary, the system required 30–40 minutes for the temperatures to stabilize and an initial bake-out period for the new polymer to be fully functional. The fluorescent intensity of the polymer varied from capillary to capillary, and observed counts ranged between 5,000,000 and 150,000 in our tests. Capillaries exhibiting counts below 200,000 were considered substandard and unusable. The system was considered ready when the baseline signal did not drift more than 0.2% in two minutes.

The Vapor Tracer[2] required about 30 minutes for internal components to heat to 190°C from a cold start. Once the system had achieved operating temperature, one sampling and analysis cycle prepared the system for useful measurements. The most frequent maintenance item is replacement of the silicone membrane, where monthly service is recommended. Replacement of the membrane was simple and took less than five minutes. After replacement the system took an hour or two before becoming fully operational. This time is appreciably longer than the cold start time because the system has been fully vented to the atmosphere during membrane replacement. Other user maintenance items include renewing the internal drying molecular sieves, methylene chloride reagent gas diffusion tubes, and an internal time standard (BHT) gas diffusion tube. The molecular sieves can be replaced when servicing the membrane. The internal gas diffusion tubes are purported to remain viable for up to one year. These items were not serviced during our five-week test of the unit.

The zNose GC/SAW required 30–60 minutes to become operational from a cold start. This system uses UHP helium for pneumatic control and as the carrier gas for the gas chromatograph. The helium is purchased in small metal gas cylinders that contain sufficient volume for two to three days of operation. Handling of the gas cylinder is straightforward. Once gases and power are applied to the system, the external data system is required to connect to the detector unit. This is accomplished by clicking an icon in the software main control panel. In most cases the connectivity is established within seconds; however, on several occasions, lengthy delays were encountered because of communications failures.

With communications established, several sensor components are required to reach the temperature set points. The necessary temperatures were normally reached in less than a half hour. Several baking events were needed prior to using the instrument. The system stabilized more quickly if the trap was cleaned several times followed by several baking cycles applied to the SAW detector. Subsequently, numerous full analytical cycles (in repeat mode using the headspace over methanol or other solvent) were needed to further clean the system. Typically ten full cycles were performed. In later cycles the system exhibited low background signal noise across the spectrum of the chromatogram and thus was determined to be ready for a sample of analytical interest. If the system was not used for more than thirty minutes, several full cycles were required to re-establish analytical conditions.

The zNose system appeared to be susceptible to contamination, and we found that great care must be taken to keep the injector scrupulously clean. In addition, we experienced difficulties clearing the instrument of samples containing high concentrations of either analytes or interferents. However, once the system was clean and stabilized, many samples could be analyzed quickly at relatively high sensitivity. Other than the cleaning requirements, there are no daily maintenance needs.

Failure and Recovery

A complete failure analysis for each of the sensors evaluated is beyond the scope of this evaluation. However, we will present our experiences with system failures during the time that the devices were under review.

Two FIDO sensors were obtained for evaluation. One system was based on dual-wavelength detection in an attempt to provide molecular speciation information. This system exhibited an unusually high level of noise (±2.0% quench), which was attributed to an electronic malfunction. Therefore, no tests were performed with this instrument. A second single-channel sensor did not exhibit excessive noise and was used for all evaluations. This sensor had one component

failure in which wiring that supports the heating element was compromised. Nomadics promptly sent a replacement inlet. and no further problems were encountered.

We experienced no instrumental failures with the Vapor Tracer[2] detector during our evaluation period. The system always responded in a predictable manner. and the data system was extremely stable.

During our evaluations the zNose sensor had a catastrophic failure when the cooling mechanism of the SAW failed. The SAW assembly was removed and shipped to EST, who sent a replacement assembly two days later. Installation of the SAW detector was relatively simple. Prior to operation, several changes in settings on the instrument were made under the direction of EST personnel, requiring approximately 30 minutes of telephone interaction.

8   ASSESSMENT AND RECOMMENDATIONS

We investigated a broad range of chemical vapor detectors for point-source detection for this report. Based on our initial, broad-range assessment, specific detectors were identified and subjected to further evaluations, including in-house laboratory testing. The five candidates selected for detailed follow-on investigations were:

- Vapor Tracer[2] from GE Ion Track;
- FIDO from Nomadics;
- zNose 4100 from Electronic Sensor Technology;
- Ion Trap Detector from Varian; and
- EGIS II/III from Thermo Detection.

The conclusions of our testing and evaluation, including advantages and disadvantages of the detectors and relative ranking, are discussed below.

The GE Ion Track Vapor Tracer[2] IMS was the most sensitive and selective of the detectors we evaluated. The detector appears to be highly durable and has sampling characteristics (sampling rate and sample size) that are favorable to point-source detection. The system is operated by a mature data and control system and requires very limited maintenance during operation. In addition, the Vapor Tracer[2] detector has the potential for greater sensitivity by implementing relatively simple modifications to the sample preconcentration module.

The Nomadics FIDO was the second most sensitive detector of those we investigated. To achieve the sensitivity reported in the scientific and marketing literature, the polymer temperature was reduced to 40°C. At this temperature the full analytical cycle time (time between measurements) was increased to two minutes. Overall, we found the FIDO detector to be small, lightweight, and simple to operate. However, FIDO has difficulties with common airborne contaminants such as diesel and gasoline exhaust and therefore may be of limited utility during range surveys.

The zNose 4100 from Electronic Sensor Technology was the least sensitive of the detectors evaluated in our laboratory tests. The relatively low sensitivity was attributed, in part, to the detector's slow sampling rate. The zNose detector did not respond to gasoline exhaust; however, diesel exhaust caused the internal SAW microbalance to shut down. The detector was the largest of those tested and required a constant source of UHP helium.

The Ion Trap Mass Spectrometer is an extremely sensitive and versatile detector that is often used as a vapor sensor. However, this system is highly complex and does not yet contain an integrated explosives sampling assembly. The absence of an integrated explosives sampling assembly was the primary factor that precluded laboratory testing.

The EGIS II/III from Thermo Detection has a stated detectability of 50 pg for TNT. This value was the least sensitive of the reported values. The EGIS detector is comparatively large and is configured as a laboratory detection system. Therefore, the system is more compatible with operation from a benchtop than from a portable field sampling device. An additional complication with this detector is the need for a constant source of UHP helium.

Based on our comprehensive explosives detector evaluations, the Vapor Tracer[2] detector is recommended for further laboratory and field testing. The principal objective for additional tests will be to characterize the response of this detector in proximity to various configurations of explosives chunks and high-concentration soils.

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APPENDIX A: COMMERCIAL SENSORS REVIEW

Manufacturer	Model	Code	Contact	Methodology	Detection limit
Barringer	Centurion	IMS	Yes	Ion mobility MS	ppmv
	Chemical warfare / toxic gases / wall mounted unit (malls, public facilities) / continuous monitor / no preconcentration				
Barringer	Sabre	IMS	Yes	Ion mobility MS	3000 pg (TNT)
	Hand-held / gas sampling 1.0 LPM 3-s max / sample trapped on proprietary coated metal / Ni63 ionization / IMS detection / detection based on explosive on particle trapped on sampling screen				
Barringer	IonScan	IMS	Yes	Ion mobility MS	300 pg (TNT)
	Bench top particulates only / wipe samples only / size of microwave oven / detection based on explosive on particle trapped on sampling screen				
Barringer	Sentinel	IMS	Yes	Ion mobility MS	300 pg (TNT)
	Walk-through / dual-stage, high-volume samplers - on metal / 300 ccm into detector / mass detection limit not known, but same IMS component is used - estimate 300 pg (same as IonScan)				
Electronic Sensor Technology	zNose4100	GC/SAW	Yes	Gas chromatography/surface acoustic wave	10 pg
	Small bench-top / gas sampling onto TENAX (other materials have been used), standard 30 ccm and 30-s sampling time, thermal desorption and 10-s GC analysis / some compounds detected at 1 pg / detector has no inherent selectivity / highly susceptible to interferences / compatible with manual high volume sampler				
Extrel	Merlin Magic	Q-MS	Yes	Quadrupole MS	10 ppbv
	Real-time gas analysis systems / Merlin Magic (Extrel also has custom line of MS analytical instruments)				
Graseby		GC/ECD	Yes	Gas chromatography/electron capture	
	Discontinued Product				
Graseby		IMS	Yes	Ion mobility MS	
	Converted to chemical warfare (CW) agents / Graseby products in general were converted to military (CW) applications / IMS for CW uses lower ionization/drift tube temperature than explosives - 105ºC (less power - military field use)				
IDS	Orion Plus	GC/IMS	Yes	Gas chromatography ion mobility MS	
	Discontinued/recalled-service issue				
IDS	Sirius	GC/IMS	Yes	Gas chromatography ion mobility MS	
	Discontinued/recalled-service issue				
IDS	Orion Mail	GC/IMS	Yes	Gas chromatography ion mobility MS	
	Discontinued/recalled-service issue				
IDS	Orion	GC/IMS	Yes	Gas chromatography ion mobility MS	
	Discontinued/recalled-service issue				

Manufacturer	Model	Code	Contact	Methodology	Detection limit
GE Ion Track		GC/ECD	Yes	Gas chromatography/electron capture	
Discontinued product					
GE Ion Track		GC/IMS	Yes	Gas chromatography/ion mobility spectrometer	
Discontinued product					
GE Ion Track	VaporTracer[2]	IMS	Yes	Positive/negative ion mobility MS	10 pg (TNT)
Hand-held / 4-L/min sampling rate / unique positive-negative ion extraction					
GE Ion Track	ITEMISER	ITMS	Yes	Positive/negative ion mobility MS	10 pg (TNT)
Bench top / particulates					
GE Ion Track		GC/ECD	Yes	Gas chromatography ion mobility MS	
Discontinued product					
MSA Instrument		FIS	No	Field ion MS	
Mine Safety Appliances Company has stopped development of the "Field Ion Spectrometer"					
Nomadics FIDO (IV)		QFP	Yes	Quenched florescent polymer	0.1 pptv
NVESD is working with this device.					
NUSS	Explorer2000	NLDM	Yes	Nonlinear drift ion mobility MS	
Sun Nuclear / Small hand held unit / nonlinear dependence of ion mobility in an electric field / in testing / not expected to be more sensitivity than IMS / uses Ni63 source					
ORNL		ITD	Yes	Ion trap MS	500 fg (est)
Spoke with ORNL ion trap researcher / some ITD explosives work / mostly negative ion CI (MeOH) / some work with glow discharge / direct capillary inlet (0.5 L/min) / Varian Instrument with turbomolecular pump - shaker table tested / detection high femtogram fg / submitted several proposals for ~500K$ for ITD explosive studies / preconcentration would likely be required / ideas on sampling, e.g., heating with shroud / currently working on build-out of ITD system mounted in Humvee and light armored vehicles for chemical warfare agent detection					
Scintrex		TR	Yes	Thermal redox	9 ppbv (TNT)
Hand-held					
Thermo Detection	EGIS II/III	GC/CL	Yes*	Gas chromatography chemiluminescence	50 pg
All samples collected onto polymer sampling pad / vapor samples pulled through polymer with hand-held air sampler / pad transferred to analyzer / 4-s GC run / EGIS III cryofocused GC / chemiluminescence detection-special unit for EGIS systems					
Tri-Corders		ITD	Attempted	Ion trap MS	
Viking		GC/Q-MS	No	Gas chromatography Q-MS	ppbv
XID		GC/ECD	No	Gas chromatography/electron capture	

APPENDIX B: HENRY'S LAW CONSTANT VALUES

Desired conc. vapor (ppb)	Temp. (K)	MW	Conv. factor	Conc. vapor (G/mL)	Henry's con. (g/mL / g/mL)	Soln. conc.
2,4-DNT over aqueous solutions						
1	295	182	8.20E+10	7.52E–12	3.80E–05	0.198
2	295	182	8.20E+10	1.50E–11	3.80E–05	0.396
5	295	182	8.20E+10	3.76E–11	3.80E–05	0.99
7	295	182	8.20E+10	5.27E–11	3.80E–05	1.39
8	295	182	8.20E+10	6.02E–11	3.80E–05	1.58
10	295	182	8.20E+10	7.52E–11	3.80E–05	1.98
20	295	182	8.20E+10	1.50E–10	3.80E–05	3.96
25	295	182	8.20E+10	1.88E–10	3.80E–05	4.9
40	295	182	8.20E+10	3.01E–10	3.80E–05	7.9
50	295	182	8.20E+10	3.76E–10	3.80E–05	9.9
80	295	182	8.20E+10	6.02E–10	3.80E–05	15.8
100	295	182	8.20E+10	7.52E–10	3.80E–05	19.8
120	295	182	8.20E+10	9.03E–10	3.80E–05	23.8
200	295	182	8.20E+10	1.50E–09	3.80E–05	39.6
2,4,6-TNT over aqueous solutions						
1	295	227	8.20E+10	9.38E–12	5.52E–07	17.000
1.5	295	227	8.20E+10	1.41E–11	5.52E–07	25.500
1.64	295	227	8.20E+10	1.54E–11	5.52E–07	27.880
2	295	227	8.20E+10	1.88E–11	5.52E–07	34.000
5	295	227	8.20E+10	4.69E–11	5.52E–07	85.000
7	295	227	8.20E+10	6.57E–11	5.52E–07	119.001
8	295	227	8.20E+10	7.51E–11	5.52E–07	136.001
10	295	227	8.20E+10	9.38E–11	5.52E–07	
25	295	227	8.20E+10	2.35E–10	5.52E–07	
50	295	227	8.20E+10	4.69E–10	5.52E–07	
100	295	227	8.20E+10	9.38E–10	5.52E–07	

REPORT DOCUMENTATION PAGE

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1. REPORT DATE (DD-MM-YY) April 2004	2. REPORT TYPE Technical Report	3. DATES COVERED (From - To)

4. TITLE AND SUBTITLE

Point-Source Energetics Detection: Initial Sensor Evaluation

5a. CONTRACT NUMBER

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)

Neal E. Van Wyck and Philip G. Thorne

5d. PROJECT NUMBER

5e. TASK NUMBER

5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

U.S. Army Engineer Research and Development Center
Cold Regions Research and Engineering Laboratory
72 Lyme Road
Hanover, NH 03755-1290

8. PERFORMING ORGANIZATION REPORT

ERDC/CRREL TR-04-10

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

10. SPONSOR / MONITOR'S ACRONYM(S)

11. SPONSOR / MONITOR'S REPORT NUMBER(S)

12. DISTRIBUTION / AVAILABILITY STATEMENT

Approved for public release; distribution is unlimited.

Available from NTIS, Springfield, Virginia 22161.

13. SUPPLEMENTARY NOTES

14. ABSTRACT

The development of real-time detection capability for explosives and propellants in high-concentration point sources is an important objective for comprehensive test and training range management. This report documents efforts to identify and characterize sensors that are both sensitive and selective to high-concentration point sources and can operate in a standoff mode by detecting the vapors released by energetics. Other factors under study included portability, speed of analysis, and overall system ruggedness. Initial evaluations identified 28 potential detection systems. Based primarily on sensitivity requirements, the initial list was reduced to five candidate detectors. The subset of detectors was then subjected to further evaluation, including extensive laboratory testing. Based on the results of laboratory testing and evaluations, we identified a single detector that warrants further investigation: GE Ion Track's Vapor Tracer[2]. The Vapor Tracer[2] is the most sensitive of the detectors tested and has the greatest freedom from interferences. We recommend follow-on laboratory and field investigations to determine the potential of this detector for high-concentration point-source detection.

15. SUBJECT TERMS

Detection	Propellants
Explosives	Sensors

16. SECURITY CLASSIFICATION OF:

17. LIMITATION OF ABSTRACT

18. NUMBER OF PAGES

19a. NAME OF RESPONSIBLE PERSON

a. REPORT	b. ABSTRACT	c. THIS PAGE			19b. TELEPHONE NUMBER (include area code)
U	U	U	U	28	